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CHEMILUMINESCENCE FROM ORGANIC REACTIONS FORMATION OF
DIPHENOYL PEROXIDE AS AN INTERMEDIATE(U) ILLINOIS UNIV
AT URBANA DEPT OF CHEMISTRY C B LITTLE ET AL
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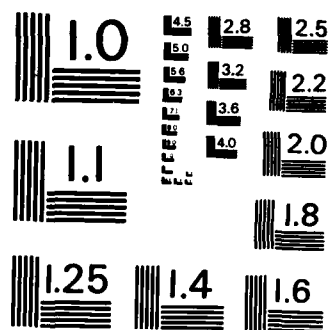
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N0014-76-C-0745-39	2. GOVT ACCESSION NO. AD-A159144	3. RECIPIENT'S CATALOG NUMBER Technical
4. TITLE (and Subtitle) Chemiluminescence from Organic Reactions. Formation of Diphenoyl Peroxide as an Intermediate.		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) Charles B. Little and Gary B. Schuster		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Illinois Urbana, Illinois 61801		8. CONTRACT OR GRANT NUMBER(s) C N0014-76-0745
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Program, Materials and Science Division Office of Naval Research, 800 N. Quincy Street Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-616
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 30, 1985
		13. NUMBER OF PAGES 26
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) chemiluminescence diphenoyl peroxide		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Visible, long-lasting chemiluminescence results when diphenic anhydride and p-nitroperoxybenzoic acid in THF are treated with powdered KOH in the presence of a catalytic chemiluminescence (CIEEL) activator. This chemilumi- nescent process is presumed to involve <u>in situ</u> generation of diphenoyl peroxide, which then undergoes chemiluminescent decomposition by the CIEEL mechanism. Carboxylate 4, the precursor to diphenoyl peroxide in this reaction, was generated by an entirely different route from peroxide 5.		

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OFFICE OF NAVAL RESEARCH

Contract N0014-76-C-0745

Task No. NR-051-616

TECHNICAL REPORT NO. N0014-76-C-0745-39

Chemiluminescence from Organic Reactions. Formation
of Diphenoyl Peroxide as an Intermediate.

by

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Prepared for Publication

in

Journal of Organic Chemistry

School of Chemical Sciences

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Urbana, Illinois 61801

August 30, 1985

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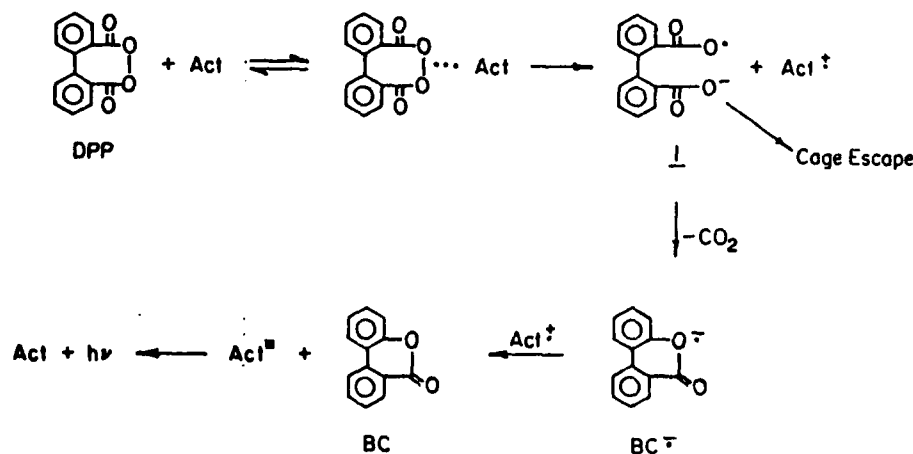


In 1978 we fully delineated the chemically initiated electron-exchange (CIEEL) mechanism based upon our detailed investigation of the chemiluminescent decomposition of diphenoyl peroxide (DPP, Scheme 1)¹. Since then our research in chemiluminescence has focused on exploring the scope of the CIEEL mechanism in other classes of organic peroxides, including dioxetanes,² dioxetanones,³ endoperoxides,⁴ secondary peroxyesters⁵ and malonyl peroxides.⁶ Nevertheless, the efficiency of excited singlet state production from DPP by the CIEEL mechanism remains among the highest of all known chemiluminescent reactions⁷ and so has sustained our interest in this system.

The origin of this efficiency lies in the unique ability of the radical anion 1 to rearrange rapidly to a much stronger reductant, benzocoumarin radical anion ($BC^{\cdot-}$), which then undergoes exergonic annihilation with Act^{\dagger} before cage escape.¹ We reasoned, therefore, that alternate generation of 1 from a suitable precursor might provide a chemiluminescent reaction of comparable efficiency without the need to prepare and isolate DPP.

In the course of our recent research along these lines, we discovered a potentially useful chemiluminescent process that appears to proceed by in situ generation of DPP from comparatively stable and non-hazardous starting materials.

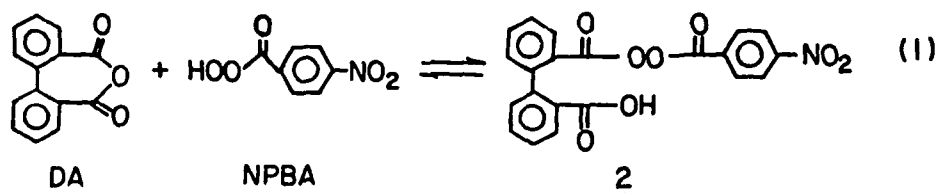
Scheme I



Act = Catalytic Chemiluminescence Activators

Results

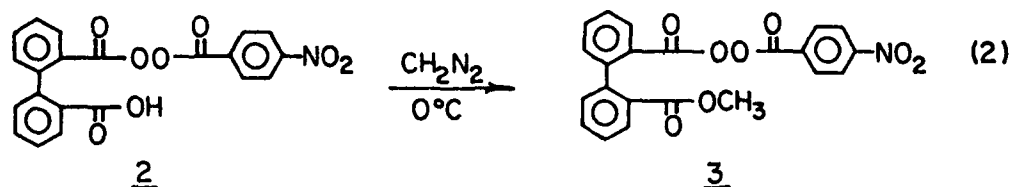
Preparation and Characterization of Peroxide 2. The reaction between a carboxylic anhydride and a peroxyacid forms the basis of a well known synthesis of unsymmetrical diacyl peroxides.⁸ We find that such a reaction readily occurs, at room temperature and without catalyst, when diphenic anhydride (DA) and p-nitroperoxybenzoic acid (NPBA) are mixed in equal amounts (10^{-3} to 10^{-2} M) in THF. FT-IR analysis shows that the absorption bands of the starting materials are immediately diminished; superimposed on them are new bands characteristic of a diacyl peroxide (1775 , 1795 cm^{-1})⁹ and a simple carboxylic acid (1728 cm^{-1}), consistent with the structure of the expected product, **2** (eq. 1). For short periods thereafter, no change in the IR spectrum is evident, but at longer



times (12 to 72 h depending on solvent purity) **2** begins slowly to disappear and DA partially to reappear, as the solution gradually becomes non-peroxidic. Since NPBA solutions undergo spontaneous decomposition on the same time scale, we infer that **2** exists in equilibrium with starting materials and is gradually depleted as the NPBA is depleted.

As a consequence of this equilibrium, **2** cannot be isolated in pure form. Nevertheless, its identity rests firmly on its IR spectrum and on the isolation of its methyl ester, **3**, prepared in moderate yield by treatment of freshly prepared

solutions of 2 with diazomethane at 0°C (eq. 2). Peroxide 3 was thus obtained as a stable, crystalline solid (mp 111°C, dec) whose full characterization is included in the Experimental Section.



Injection of 2 onto a GC column (280°C) results in formation of benzocoumarin in as high as 40% yield. Adding excess triphenyl phosphine before GC assay suppresses benzocoumarin formation and causes DA to reappear almost quantitatively. Though the mechanism of this thermal generation of benzocoumarin remains obscure, it is sufficient to note that it is too slow at 25°C to produce any measurable quantity of this substance in 24-72 h.

Finally, we observe that 2 disappears faster in solutions containing perylene or rubrene, typical chemiluminescence activators in the CIEEL process,¹ but again without benzocoumarin formation at room temperature. In a separate experiment we determined that these compounds are consumed in a reaction with NPBA, thereby depleting NPBA, and 2, faster than we would otherwise expect. We specifically rule out electron transfer induced decomposition of 2 under these conditions on the grounds that this would lead to rapid O-O bond scission¹⁰ and, ultimately, benzocoumarin formation. Moreover, we find that peroxide 3 is entirely unaffected by these activators at 25°C in solution, indicating that the diacyl peroxide moiety in this compound (and by inference, 2 as well) is incapable of oxidizing the activators we used under these conditions.

Chemiluminescent Decomposition of 2. Solutions of 2 containing perylene or rubrene display a barely detectable chemiluminescence at room temperature. However, the further findings that solutions of NPBA containing these activators also display this low-level chemiluminescence and that addition of DA does not enhance it, allow us to rule out any direct involvement of 2 in this minor light generating reaction.

Immediately upon adding dry, powdered KOH to a solution of 2 (ca. 10^{-2} M) containing a CIEEL activator (ca. 10^{-3} M) we observe a rapid buildup and then a slow decay of chemiluminescence intensity (Figure 1). Under these conditions this chemiluminescence is readily visible to the naked eye and typically remains so for 30 to 60 min in a darkened room. In each case the chemiluminescence corresponds to fluorescence from the activator. While the heterogeneity of the system introduces a degree of irreproducibility, the curve shown in Figure 1 is broadly representative of the chemiluminescent behavior we observe when the reaction is carried out as described above. Vigorous stirring to keep solids suspended changes neither the rates of buildup and decay, nor the maximum chemiluminescence intensity reached.

To observe chemiluminescence in this system, DA, NPBA and KOH can be mixed in any order in the presence of an activator, but chemiluminescence buildup only commences when all of these ingredients are in contact in solution.¹¹ If the activator is added to the other three ingredients at a later time (Figure 2) we observe that the buildup and decay of some chemiluminescent intermediate proceeds anyway, but that this intermediate appears to live longer in the absence of the

activator. Significantly, we find that other peroxyacids (e.g., MCPBA), but not anhydrous hydrogen peroxide, can be substituted for NPBA in this chemiluminescent process.

Acting on the hypothesis that KOH initiates the chemiluminescence buildup by forming the potassium carboxylate from 2, we investigated the effect of 18-crown-6 on this system. As shown in Figure 3, the peak chemiluminescence intensity approximately triples (1.3×10^6 vs 4.1×10^6) in the presence of a 6-fold excess of 18-crown-6, but this peak is still reached at the same time for both solutions. Furthermore, a solution of 18-crown-6 treated with KOH and then filtered does not induce chemiluminescence when added to 2 and an activator. This suggests that the principle effect of the crown ether is to solubilize a potassium carboxylate and not to solubilize KOH directly.^{12,13}

The effect of the chemiluminescence activator was probed to determine whether chemiluminescence might be occurring by a classical energy transfer mechanism rather than by the CIEEL mechanism. Treating 2 with KOH in the presence of 9,10-diphenylanthracene (DPA, $E_s = 72$ kcal/mol) results in easily detected chemiluminescence, but under identical conditions we detect no chemiluminescence whatsoever when 9,10-dibromoanthracene (DBA, $E_s = 72$ kcal/mol) is employed as the activator. Even taking into account the difference in fluorescence efficiencies ($\phi_F = 0.8$ for DPA, 0.1 for DBA), energy transfer to these compounds under the conditions we used would have resulted in easily detected chemiluminescence from both, not just from DPA. The results argue strongly in favor of the CIEEL mechanism and against energy transfer sensitization.

Several other insoluble bases are also capable of initiating this chemiluminescent reactions. The heterogenous conditions make comparisons among these bases difficult, but some distinct trends are noted. In parallel experiments with equimolar quantities of the alkali metal hydroxides, NaOH produces substantially lower chemiluminescence intensity than does KOH, while LiOH produces still less (Figure 4). Inclusion of excess 15-crown-5 in the solution treated with NaOH results in greatly enhanced chemiluminescence intensity, but the light yield in this circumstance is still lower than that from KOH treatment without a crown ether. Again, rapid stirring of these solutions during the reaction does not alter rates of buildup and decay or the peak intensity reached. Substantially the same results are obtained with the hydride reagents, KH, NaH and LiH: KH induces much higher chemiluminescence intensity than does NaH or LiH.

Solutions of 2 treated with KOH or KH retain a milky appearance even after filtration and centrifugation. In contrast, similar solutions treated with the sodium or lithium bases can easily be clarified by filtration after the bases are allowed to settle out. We are thus able to demonstrate, using NaOH and LiOH, that chemiluminescence activity does not require continued contact with suspended solids.

Benzocoumarin Formation in Chemiluminescence Experiments. Benzocoumarin is the principle product of both the thermal and CIEEL decompositions of DPP. We find that benzocoumarin is also formed from 2 by treatment with solid bases, and in yields that parallel the chemiluminescence yields we observe. Typically, KOH or KH produce 25% to 40% yields while LiOH or LiH produce only ca. 5% (based on diphenic anhydride initially present). The presence of a CIEEL activator increases these

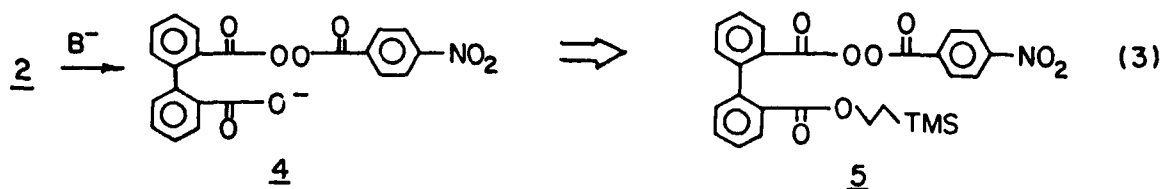
yields, but only marginally. Thus, while the principle route to benzocoumarin formation may not involve bimolecular reaction with the CIEEL activator, at least some of the benzocoumarin appears to be formed by the CIEEL path.

Comparison with Chemiluminescence from DPP. We previously reported that, for DPP, the chemiluminescence intensity is directly proportional to the concentration of the peroxide at any fixed activator concentration.¹ Thus we can estimate an upper limit on the concentration of any chemiluminescent intermediate produced from 2 if we make the reasonable assumption that such an intermediate would be less than or equal to DPP in its light generating efficiency by the CIEEL process.

At an activator concentration of 10^{-3} M we observe a chemiluminescence intensity from 10^{-2} M DPP that is approximately 500 times higher than the peak intensity from a 10^{-2} M solution of 2 treated with KOH. We estimate from this result that the chemiluminescent intermediate formed from 2 never exceeds a concentration of ca. 2×10^{-5} M, well below the limits of detectability by our FT-IR technique.

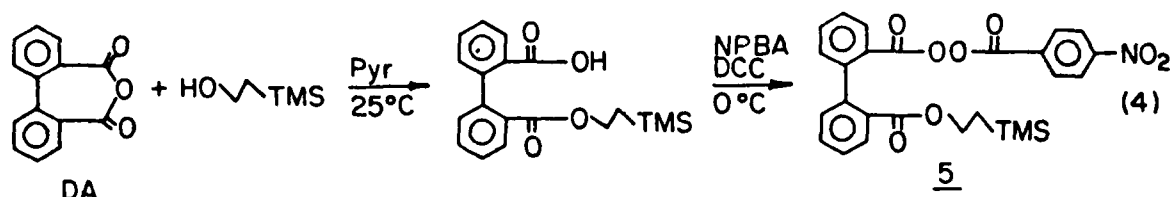
We find that authentic DPP is rapidly destroyed under the harsh reaction conditions required to generate chemiluminescence from 2. Thus, any similarly labile intermediate formed from 2 would not be expected to build up to detectable levels.

Preparation of Peroxide 5. To test the idea that formation of the carboxylate, 4, is minimally required to produce chemiluminescence, we chose to exploit the fluoride-induced deprotection of 2-TMS ethyl esters¹⁴ as in equation 3. This approach we especially appealing in that the required peroxide 5,



was expected to be at least as stable as peroxide 3 and the conditions generally used for deprotection are mild by comparison with those used to generate chemiluminescence from 2.

Peroxide 5 was obtained in virtually quantitative crude yield in two steps from diphenic anhydride (eq. 4). Indeed, in its pure state this crystalline solid



is stable indefinitely at room temperature and shows only slow decomposition at its melting point. In THF solution it is likewise stable, suffering no decomposition (by FT-IR) even after 48 h at room temperature.

Chemiluminescent Decomposition of Peroxide 5. Treatment of 5 with fluoride ion in the presence of perylene does result in easily detected chemiluminescence, but the choice of the fluoride source is critical to the success of the reaction. We find that the sparingly soluble benzyl trimethyl ammonium fluoride (BTAF)¹⁵ is the preferred reagent. Upon adding a solution of 5 and perylene to finely powdered BTAF we observe a rapid build up of chemiluminescence intensity to a low but rather constant level (Figure 5a). Unlike the reaction of KOH with 2, the reaction of BTAF with 5 is highly sensitive to mechanical mixing: the faster the mixing, the

faster the build up and decay of chemiluminescence and the higher the peak intensity. At high concentrations of **5** and perylene (ca. 10^{-2} M) and using an ultrasonic cleaning bath to keep BTAF dispersed in the THF, chemiluminescence is visible only briefly in a darkened room. As expected, benzocoumarin is detected among the products of this reaction. No attempt was made to optimize reaction conditions for chemiluminescence yield in this system.

Model studies with 2-trimethylsilylethyl benzoate and benzoyl peroxide show that BTAF both desilylates the ester and destroys the peroxide at comparably slow rates. Thus, even though BTAF is destructive of the diacyl peroxide moiety in **5**, the slow rate of this reaction assures that some chemiluminescent intermediate is formed from desilylation of **5** and that it survives long enough to undergo bimolecular reaction with the CIEEL activators.

The most commonly used desilylating reagent, tetra-*n*-butyl ammonium fluoride (TBAF),¹⁶ while exceptionally soluble in THF, proved to be unsuitable for our purposes. Within minutes after adding 2 equiv of TBAF to a solution of **5** and perylene, the diacyl peroxide is gone (FT-IR) and the solution gives a negative peroxide test. Thus, the short-lived chemiluminescence we observe in this circumstance (Figure 5b) appears to be a consequence of the same competition between desilylation of the ester and destruction of the diacyl peroxide that we found using BTAF, only at a much faster rate. Again using 2-trimethylsilylethyl benzoate and benzoyl peroxide in a competition experiment, we find that TBAF reacts rapidly with both compounds at comparable rates at room temperature.

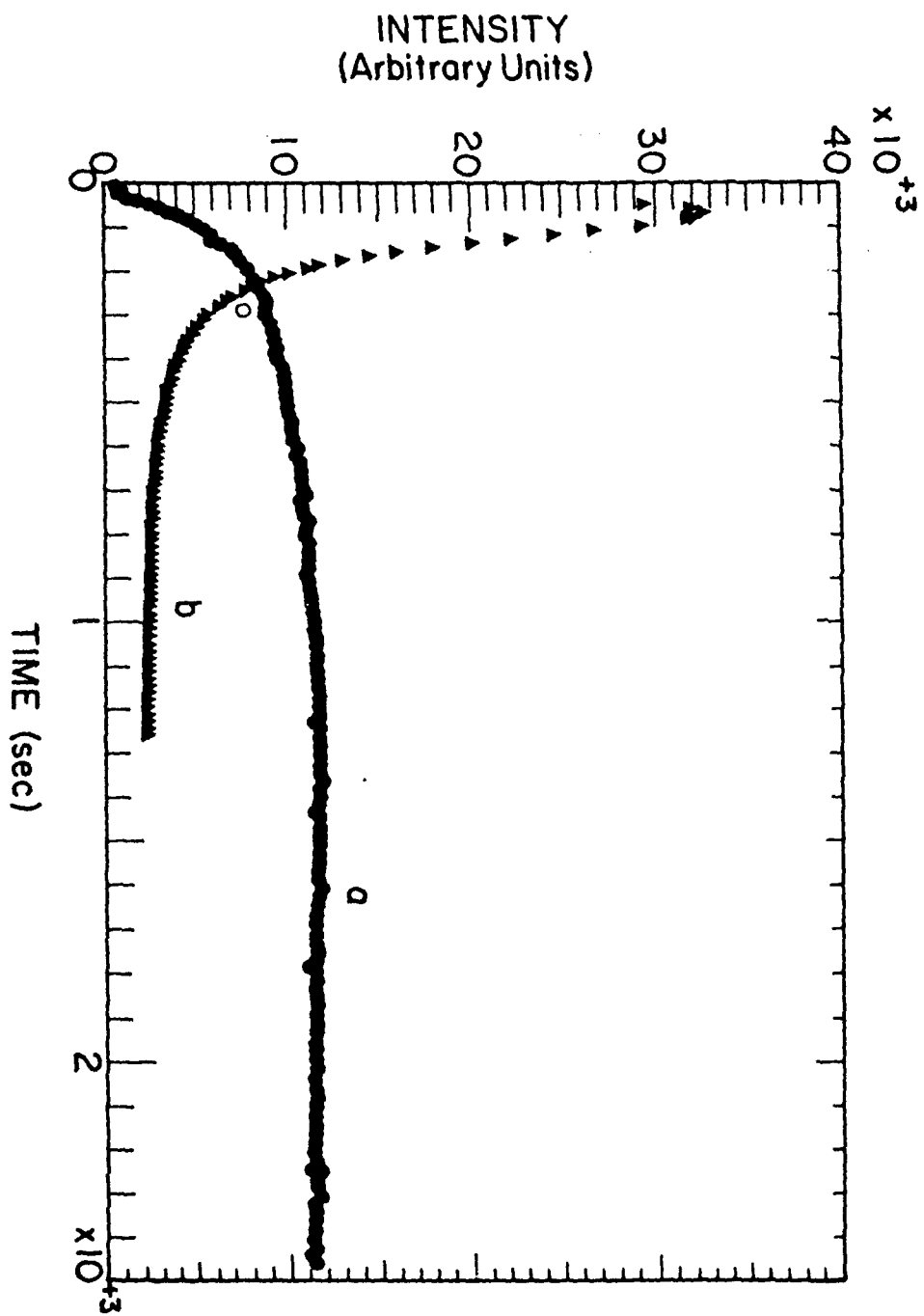


Figure 5. Chemiluminescence from a stock solution of 5 and perylene induced by 2.5 fold molar excesses of: (a) BTAF, (b) TBAF.

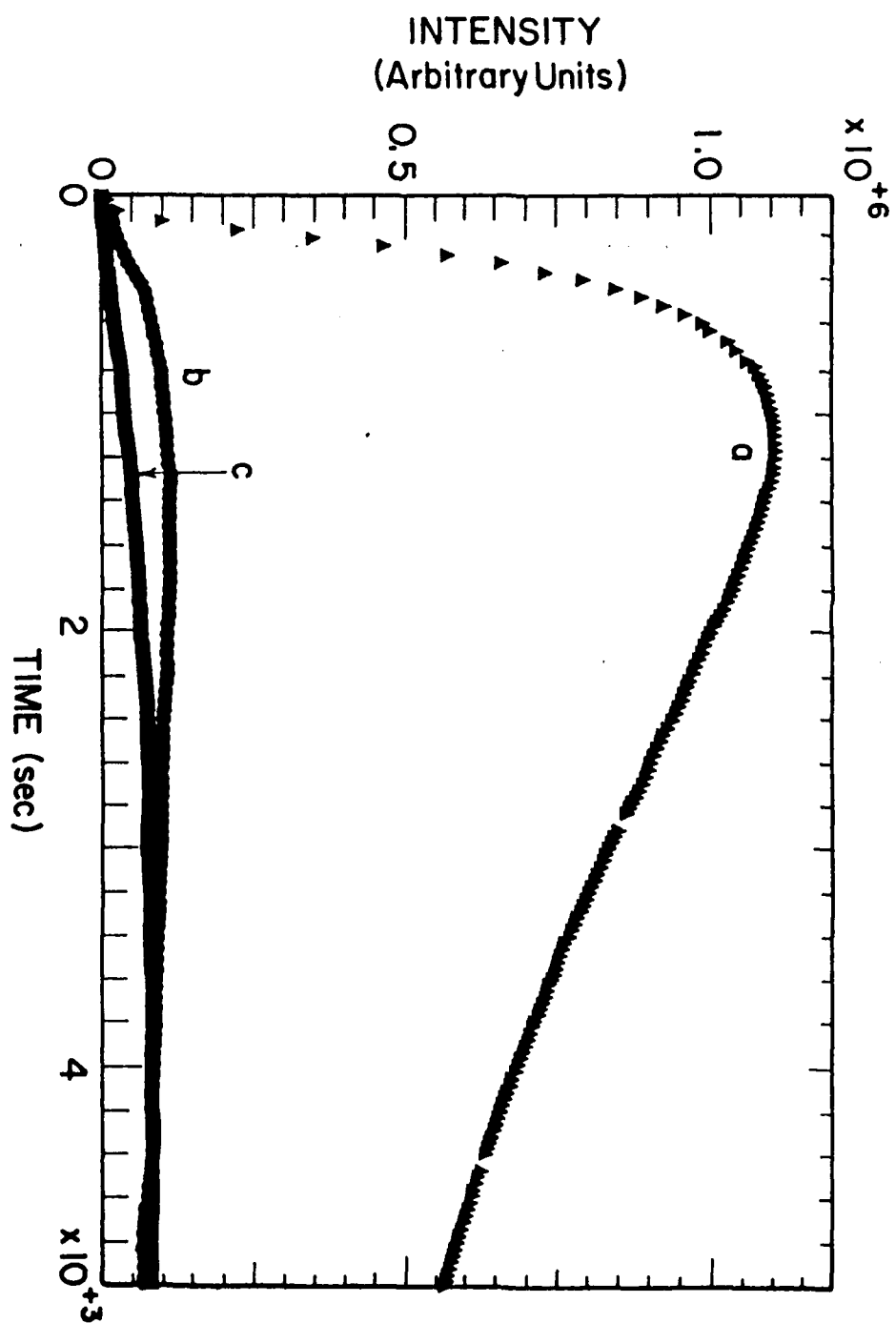


Figure 4. Chemiluminescence from 2 and perylene induced by 20 fold molar excesses of metal hydroxides: (a) KOH, (b) NaOH, (c) LiOH.

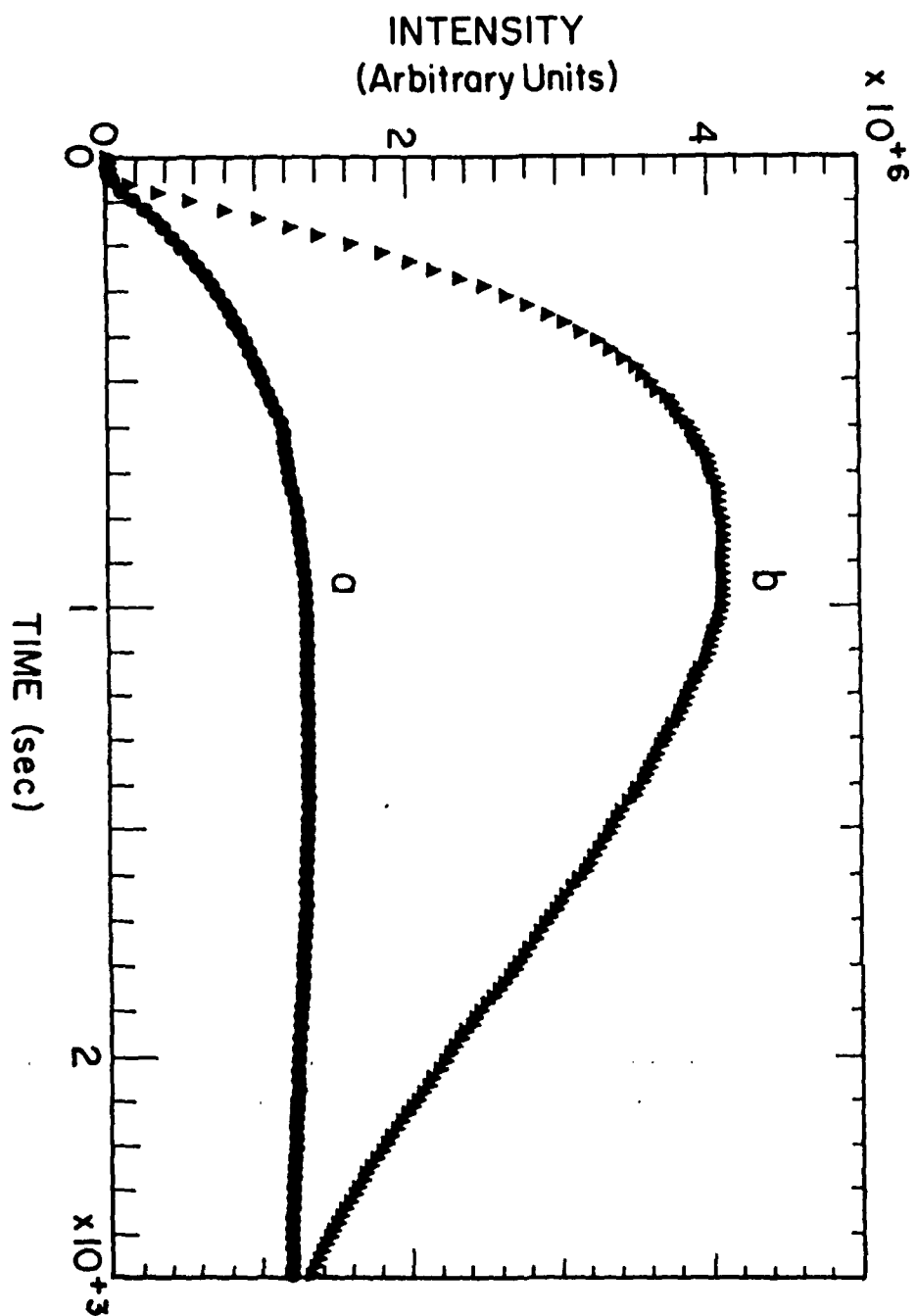


Figure 3. Effect of 18-crown-6 on chemiluminescence intensity. (a) Stock solution of 2 and perylene added to 50 mg KOH. (b) Same stock solution first added to 6-fold excess of 18-crown-6 (based on 2) then added to 50 mg KOH.

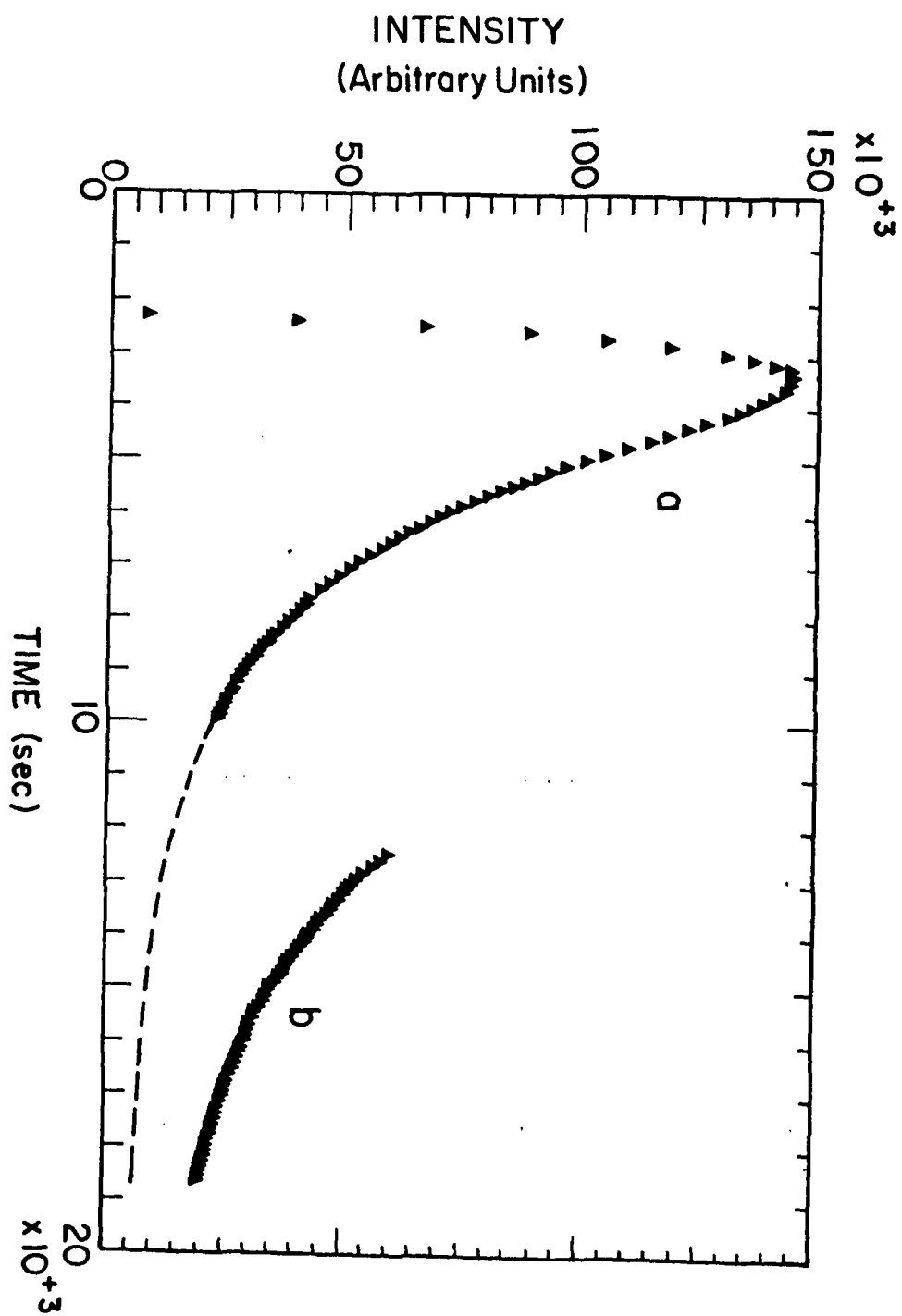


Figure 2. Effect of delayed addition of chemiluminescence activator. Solution of 2 is treated with KOH then: (a) One half is immediately added to perylene stock solution. (b) Other half of solution is added to fresh perylene stock solution after 10,000 seconds.

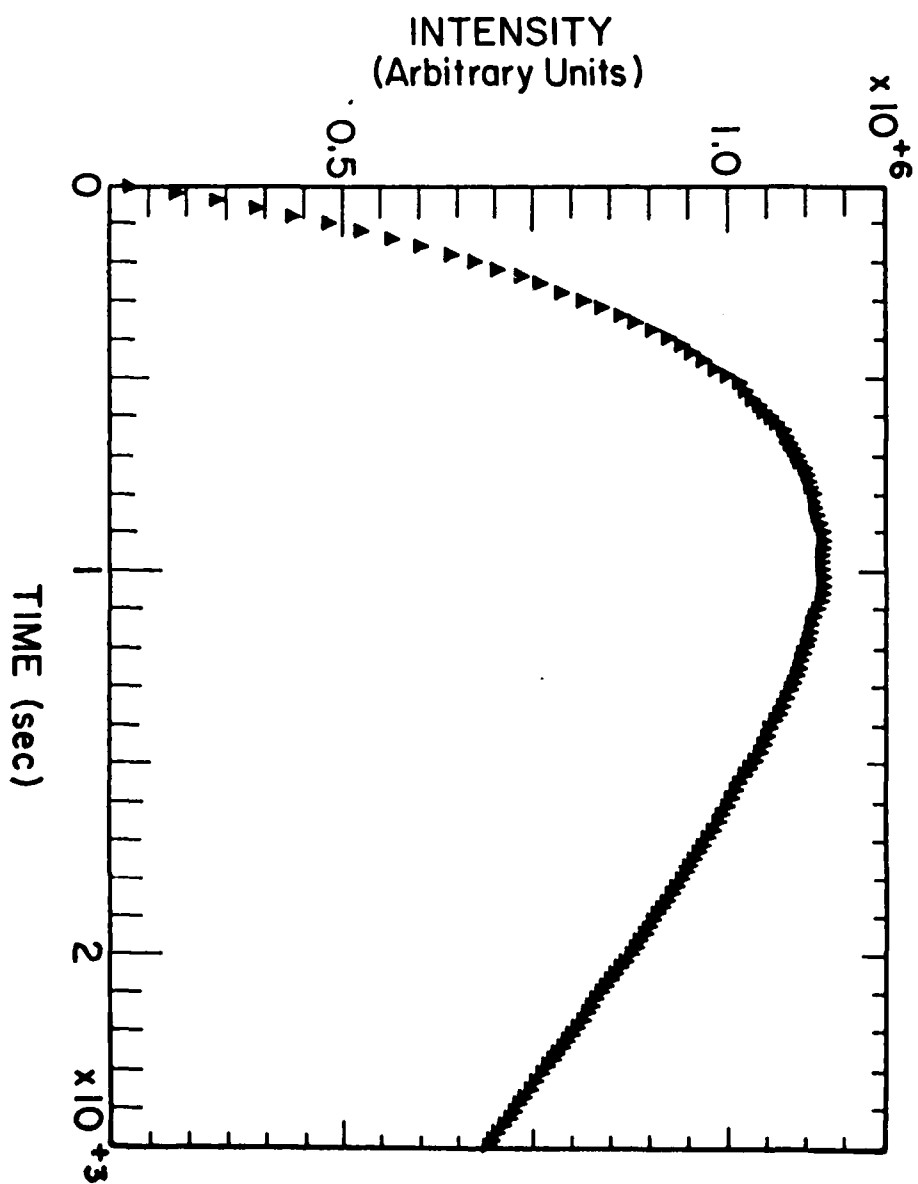


Figure 1. Typical chemiluminescence vs. time curve for a solution of 2 ($\text{ca } 10^{-2} \text{ M}$) treated with KOH in the presence of a CIEEL activator (perylene, $\text{ca } 10^{-3} \text{ M}$).

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10. See, for example: Schuster, G. B.; Schmidt, S. P. In "Advances in Physical Organic Chemistry"; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1982; Vol 18, pp 187-238, especially pp 216-218.
11. Chemiluminescence intensities are considerably lower if NPBA is treated with base before DA is added, however.
12. We are unaware of any evidence that 18-crown-6 can directly solubilize dry KOH to any appreciable extent in non-polar solvents. Crown-KOH complexes formed in alcohol solvents (ref 13) almost certainly retain alcohol molecules when dried and re-dissolved in non polar solvents. The effect of crown ethers on KOH and other salts of higher lattice energy (e.g., K_2CO_3) is probably limited

Anal. Calcd for $C_{26}H_{25}NO_8Si$: C, 61.52; H, 4.96; N, 2.77; active oxygen, 3.15. Found: C, 61.70; H, 4.90; N, 2.71; active oxygen, 3.15.

Product Analyses. Solutions from chemiluminescence experiments were diluted with 3 volumes of benzene, then treated with 1 N HCl until the small aqueous layer was <pH5. The aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL) and ether (1 x 2 mL), then checked for volatile products by gas chromatography. The combined organic phases were evaporated, leaving a residue that was fully soluble in THF for analysis by TLC, IR and gas chromatography.

Solutions containing tetraalkyl ammonium salts were treated with dry HCl gas and analyzed directly by TLC and gas chromatography. Aqueous washes were omitted owing to the ability of the onium salts to solubilize some products in water.

Acknowledgement

The authors thank Mr. Paul Cahill and Mr. Jeffrey Sternberg for many helpful discussions. This work was generously supported by the Office of Naval Research. G.B.S. is a Guggenheim Fellow.

Peroxide 5. Diphenic acid mono(2-TMS ethyl)ester was prepared by stirring diphenic anhydride (1.71 g, 7.6 mmol) with 2-TMS ethanol (2.04 g, 17.2 mmol, Petrarch Systems) in 10 mL of dry pyridine at 25°C for 50 h. FT-IR analysis of an aliquot diluted with THF showed no diphenic anhydride remaining. Removal of volatiles under vacuum left a pale green, viscous oil which crystallized slowly at 25°C. Recrystallization from hexane yielded 1.46 g (55%, 2 crops) of fine white powder: mp 87.5-88.5°C. NMR (CHCl_3 reference) δ 8.05 to δ 7.10 (m, 8H), δ 4.10 (m, 2H), δ 0.81 (m, 2H), δ -0.03 (s, 9H). IR (THF) 1728, 1712 cm^{-1} .

Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Si}$: C, 66.64; H, 6.48; Si, 8.20. Found: C, 66.72; H, 6.64; Si, 8.16.

Following the general procedure of Greene and Kazan,²² an ice-cold solution of diphenic acid mono(2-TMS ethyl)ester (822 mg, 2.4 mmol) and p-nitro peroxybenzoic acid (439 mg, 2.4 mmol) in 34 mL ether/ CH_2Cl_2 was added dropwise over 7 min to dicyclohexylcarbodiimide (500mg, 2.4 mmol) in 4 mL ether at 0°C (internal temperature). FT-IR analysis of the solution after 18 h of stirring at 0°C showed no starting material present and DCC almost completely consumed. Filtration and usual work-up yielded a light brown oil, which, upon cooling in ether/ CHCl_3 at -78°C, produced 59 mg of impure 4,4' dinitro benzoyl peroxide (mp 138°C). From the concentrated mother liquor was recovered 857 mg (70%, 2 crops) of pale yellow solid whose IR and ^1H -NMR spectra showed no trace of dicyclohexyl urea or starting materials. Recrystallization of this material from pentane at -10°C yielded analytically pure 5 as a white solid: mp 65-67°C (slow dec). NMR (CHCl_3 reference) δ 8.23 (m, $-\text{C}_6\text{H}_4\text{NO}_2$, 4H), δ 8.10 to δ 7.28 (m, 8H), δ 4.15 (m, 2H), δ 0.79 (m, 2H), δ -0.01 (s, 9H). IR (THF) 1796 and 1776 (diacyl peroxide), 1725 (ester, unresolved doublet) cm^{-1} .

Hg) at 25°C. Diphenic anhydride (Aldrich, 98%) was recrystallized from spectrograde chlorobenzene, then sublimed under vacuum. KOH pellets (Mallinckrodt, 85%) and NaOH pellets (Baker, 99%) were powdered under dry nitrogen, heated at 200°C under vacuum (0.05 mm Hg) for 24 h, powdered again and stored under dry nitrogen.¹⁸ Granular LiOH (A. D. Mackay) was powdered, then dehydrated at 150°C in a current of dry nitrogen.¹⁹ Chemiluminescence activators were chromatographed on basic alumina, then recrystallized from spectrograde solvents. TBAF (Fluka, 98%) was dried at 25°C under vacuum (0.05 mm Hg) for 48 h prior to use. BTAF (Fluka, 90%) was powdered, then dried under vacuum (0.05 mm Hg) at 25°C for 24 h then at 50°C for 24 h prior to use.^{16a} Diphenoyl peroxide was prepared by the procedure of Ramirez.²⁰ All other materials were used as received or were purified according to standard procedures²¹ when necessary.

Peroxide 3. To a cold (0°C) solution of diphenic anhydride (229 mg, 1.0 mmol) and p-nitroperoxybenzoic acid (224 mg, 1.2 mmol) in 33 mL THF was added alcohol-free²³ diazomethane (4.5 mmol) in 25 mL ice-cold ether. The resulting solution was allowed to warm to room temperature overnight, then evaporated under a stream of dry nitrogen to an oily residue which solidified under vacuum (0.05 mm Hg, 25°C). Recrystallization of this residue from pentane/ether/THF at -50°C yielded 200 mg (46%) of light yellow powder: mp 111°C (dec). NMR δ 8.22 (m, $-\text{C}_6\text{H}_4\text{NO}_2$, 4H), δ 8.14 to δ 7.27 (m, 8H), δ 3.68 (s, 3H). IR (THF) 1795 and 1775 (diacyl peroxide), 1732 (ester, unresolved doublet) cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{NO}_8$: C, 62.71; H, 3.59; N, 3.32; active oxygen, 3.80. Found: C, 62.78; H, 3.73; N, 3.10; active oxygen, 3.58.

The attractiveness of a chemiluminescent system based on in situ generation of DPP from a stable, isolable precursor inspired us to prepare and investigate peroxide 5. While this peroxide provided substantiating evidence for the mechanism shown in equation 6, it proved to be less efficient in producing chemiluminescence than the original system because of the competing destruction of the diacyl peroxide moiety by the fluoride sources we used. Considering the stability and ease of preparation of 5, we expect that a variant of this peroxide may yet be developed as a synthetically useful precursor to DPP, if not as a practical chemiluminescent system.

Experimental

General. Melting points are uncorrected. IR spectra were obtained on either a Nicolet 7003 or an IBM IR32 instrument. $^1\text{H-NMR}$ spectra were obtained on a Varian XL-200 instrument at 200 MHz in deuteriochloroform solvent using either tetramethylsilane or chloroform as internal reference. Chemiluminescence measurements were made with an EMI 9813 photomultiplier tube using 10 mm Pyrex cells fitted with Teflon stopcocks. Analytical gas chromatography was performed on a Varian 3700 series instrument (6'-5% OV-17 on Chromsorb W-HP) using either tetracosane or octadecane as an internal standard. Elemental analyses were performed by Analysis Laboratories, Urbana, Illinois.

Materials. THF (Burdick and Jackson, without preservative) was freshly distilled from sodium dispersion-benzophenone under nitrogen for all chemiluminescence experiments. The peroxide titre of p-nitroperoxybenzoic acid (Aldrich, 85%) was raised to 94-98% of theoretical by trituration with pH 7 buffer and then with distilled water, followed by prolonged drying under vacuum (0.1 mm

anhydrous hydrogen peroxide when it is substituted for the peroxy acids in this system, since final cyclization to DPP would not be likely in this case.

If **4** could be generated cleanly under mild conditions, we might expect it to rearrange to DPP in moderate yield. We find, however, that the harsh conditions required to generate this carboxylate from peroxide **2** are destructive of DPP and presumably of the diacyl peroxide moiety in **2** as well. While formation of DPP from **2** may thus be an inefficient chemical process, the efficiency of light production by the CIEEL mechanism assures that visible, long-lasting chemiluminescence is readily achieved.

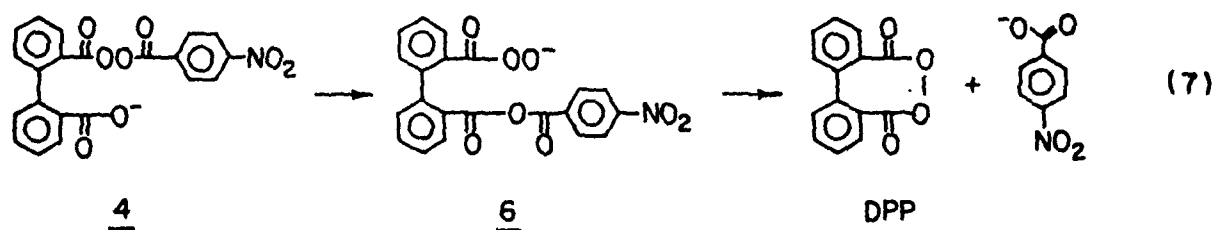
Peroxide **5** was seen as the key to improving this chemical efficiency as well as providing a test of the validity of equation 6. In this latter function we consider **5** to have served well. Chemiluminescence and benzocoumarin production are observed under conditions that unambiguously lead to deprotection of the 2-trimethylsilylethyl ester in **5**. However, the available data¹⁷ concerning nucleophilic attack of halide ions on diacyl peroxides led us to predict that this complicating reaction would not compete effectively with desilylation. Clearly it does, at least for the fluoride sources and reaction conditions we investigated, so the chemical efficiency of DPP production by this route also suffers.

Conclusion

Readily detected, long-lasting chemiluminescence is generated in a simple procedure using inexpensive, commercially available materials. Though the identity of the actual chemiluminescent intermediate was not established directly, the available data strongly suggest that diphenoyl peroxide is formed in situ and is responsible for light production by the previously described CIEEL mechanism.

the CIEEL decomposition of DPP shown in Scheme 1. While such an approach may yet prove workable in another system, it is unlikely that it is responsible for the chemiluminescence we observe here. The best evidence against it is that both peroxides 2 and 3 lack the oxidizing power to accept an electron from the CIEEL activators we used. It is thus implausible that carboxylate 4 would be a strong enough oxidant to initiate the reaction shown in equation 5. Moreover, we expect that the potassium salt of 4, formed either by KOH or KH treatment of 2, would not be appreciably soluble in dry THF except in the presence of a crown ether. Since the chemiluminescence intensity, but not the rate of its build up, is increased by crown ethers, we conclude that slow solubilization of 4 or any other salt does not adequately explain the kinetic form we observe.

Instead, our data support the more plausible explanation that the chemiluminescence results from a soluble chemical species that is formed from a slow reaction of 4, regardless of the means by which 4 is generated. The further finding that benzocoumarin is formed when we see chemiluminescence, leads us to suggest that DPP is the actual chemiluminescent intermediate. While other mechanisms may be drawn, we suggest that DPP is accessible from 4 by an acyl shift followed by cyclization of the resulting peroxy anion, 6, as in equation 6. In addition to providing an explanation for the classic consecutive reaction kinetics we observe, this shift and cyclization also account for the ineffectiveness of



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